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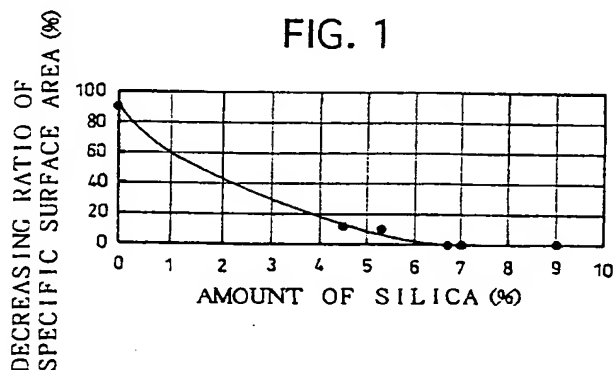
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## (54) Catalyst for purifying exhaust gas

(57) A catalyst for purifying exhaust gases, which is capable of maintaining the catalytic property and purification performance against particulates, HC, CO and NOx over a long period of time. The catalyst has a catalyst substrate and a heat-resistant inorganic oxide layer containing catalytic components, which is provided on the catalyst substrate. The heat-resistant inorganic oxide layer contains silica-doped anatase titania having a structure that 3 to 35 % by weight of silica is finely dispersed between and retained by anatase titania particles, which is an oxide obtained in the state where a silicon-containing compound and titanium-containing compound are mixed in the molecular state.



CO - precipitation

Date: 2000.11.15

## Description

BACKGROUND OF THE INVENTION1. Field of the Invention

The present invention relates to catalysts for purifying exhaust gases, and more particularly, to catalysts capable of eliminating harmful components, such as carbon monoxide (CO) or hydrocarbon (HC), contained in exhaust gases discharged from combustion furnaces, boilers, internal combustion engines or the like, especially exhaust gases discharged from diesel engines.

2. Description of the Related Art

Conventionally, exhaust gases discharged from combustion furnaces, boilers, internal combustion engines or the like have been purified by eliminating hydrocarbon and carbon monoxide therein with catalysts composed of heat-resistant ceramic particles, each having a large specific surface area, and catalytic components supported with surfaces of the heat-resistant ceramic particles. The catalysts thus arranged are always exposed to high temperature exhaust gases. So, the specific surface area of the ceramic particles is reduced and/or the particles of the catalytic components supported with the ceramic particles are enlarged, whereby the real surface area of the catalytic components is reduced so that the catalytic property deteriorates. Accordingly, there has arisen a need to develop heat-resistant ceramics capable of preventing the reduction of its specific surface area without enlarging the particles of the catalytic components supported therewith, and accordingly restraining the deterioration of the catalytic property even when used in high temperature exhaust gases over a long period of time.

Catalysts have been used to purify hydrocarbon, carbon monoxide and nitrogen oxide (NOx) contained in exhaust gases from internal combustion engines. Exhaust gases from diesel engines further contain particulates. It has been desired particularly to develop catalysts enabling sure elimination of these particulates. As the conventional catalysts for purifying exhaust gases containing particulates, trap-type (with or without catalysts) and open-type SOF decomposition catalysts have been known.

The trap-type SOF decomposition catalysts trap particulates contained in exhaust gases to restrain the discharging thereof, and are particularly effective in purifying exhaust gases containing a large amount of dry soot. This type of catalysts have, however, many problems in using them practically. Namely, regenerating devices are further needed, catalyst substrates may be cracked in the regenerating step thereof, there may occur clogging with ashes, and entire systems become complex.

On the other hand, as shown in Publication of examined Japanese Patent application No. Hei 3-38255, for example, the open-type SOF decomposition catalysts are composed of a catalyst support layer of activated alumina, for example, and oxidation catalyst of metals of the platinum group or the like, which is supported with the catalyst support layer, like the case of gasoline engines or the like. With this type of catalysts, SOF within the particulates are oxidized and decomposed along with carbon monoxide and hydrocarbon to be purified. These open-type SOF decomposition catalysts have the disadvantage that the rate of elimination of dry soot is low. But with these catalysts, no regenerating device is needed, and by improving the combustion conditions and fuel, the amount of dry soot can be reduced, so that the development of these catalysts has been investigated.

These conventional catalysts for purifying exhaust gases have, however, been incapable of reducing the amount of particulates discharged. Within high-temperature exhaust gases which causes the generation of particulates, sintering of inorganic oxide contained in heat-resistant inorganic oxide layers, and deterioration of platinum as the catalyst metal occur to decrease the catalytic property. Publications of unexamined Japanese Patent applications Nos. sho 62-149338 and 62-149339 disclose catalysts wherein titania is finely dispersed in alumina by a metal alkoxide method or coprecipitation method to enhance the heat resistance of activated alumina-based inorganic oxide layers. These alumina-based catalysts, however, may absorb sulfur compounds to form sulfate. This results in the amount of particulates discharged being not restrained sufficiently. The particulates-resorting operation has not been disclosed as an evaluation item in the above publications.

On the other hand, titania-based catalysts exhibit low adsorption against sulfur compounds so as to be discharged without changed. Therefore, it has been known that the titania-based catalysts can restrain the formation of sulfate. However, these titania-based catalysts are insufficient in heat resistance. Effective measures for enhancing the heat resistance thereof has not been known.

Summary of the Invention

It is an object of the present invention to provide a catalyst capable of maintaining its catalytic performance over a

long period of time, and a catalyst capable of maintaining its purification performance against particulates, HC, CO, NOx over a long period of time.

The present inventors have intensively researched to attain the above object. As a result, they have found a composition for a catalyst capable of maintaining its purification performance and accordingly exhibit excellent durability in high temperature atmospheres, as compared to the conventional catalysts, and have completed the present invention.

The catalyst for purifying exhaust gases with the present invention is composed of a catalyst substrate and a heat-resistant inorganic oxide layer containing catalytic components, which is provided on the catalyst substrate. The heat-resistant inorganic oxide layer contains silica-doped anatase titania having a structure that 3 to 35 % by weight of silica is finely dispersed between and retained by anatase titania particles, which is an oxide obtained in the state where a silicon-containing compound and titanium-containing compound are mixed together in the molecular state.

The silica-doped anatase titania is particularly excellent in heat resistance, and has a high specific surface area even after used over a long period of time. With this silica-doped anatase titania, the enlargement of the particles of the catalytic components is blocked and high catalytic performance can be maintained over a long period of time.

With the catalyst for purifying exhaust gases of the present invention, the heat-resistant inorganic oxide layer contains silica-doped anatase titania which is an oxide obtained in the state where 3 to 35 % by weight of silica is dispersed between and retained by anatase titania particles in the molecular state.

It is preferable that the silica-doped anatase titania contained in the heat resistant inorganic oxide layer has a structure that extremely fine silica particles on a level of an atomic order disperse between titania particles. With this structure, titania particles are prevented from sintering so as not to reduce the specific surface area. The amount of silica added to the titania particles ranges from 3 to 35 % by weight. If the amount of silica added is less than 3 % by weight, the effect of preventing sintering of titania cannot be obtained, and if the amount of silica added exceeds 35 % by weight, the sintering restraining effect is not enhanced so as to be less preferable.

Examples of the method of finely dispersing silica on an atomic level include a hydrolysis method of dispersing a mixture of alkoxide of titanium and alkoxide of silicon in titania with hydrolysis, which is performed with the present invention.

Titania has excellent SOx resistance, and has been used in exhaust gas atmospheres containing a large amount of SOx, for denitrification purpose, for example. Conventional titania without doped with silica exhibits purification ability in temperature conditions of 500 °C or less, but sintering of particles of titania occurs in temperature conditions over 500 °C such as exhaust gases from diesel engine vehicles so that the purification performance remarkably decreases. In contrast, silica-doped anatase titania of the present invention does not greatly change its crystal structure at high temperatures so as to exhibit high heat resistance. Accordingly, silica-doped anatase titania is difficult to sinter.

A heat resistance test was performed in order to exhibit heat-resistance of silica-doped anatase titania. In the heat resistance test, silica-doped anatase titania was put into an electric furnace having air at 800 °C, and a heat treatment was performed for 5 hours. Figure 1 shows the relationship between an amount of silica in silica-doped anatase titania and decreasing rate of specific surface area. Figure 2 shows the relationship between an amount of silica in silica-doped anatase titania and an increase magnification of peak strength cps on X-ray diffraction analysis with  $2\theta = 25^\circ$ .

As shown in Figure 1, when the amount of silica increases, decreasing rate of specific surface area becomes small. As shown from Figure 2, when the amount of silica increases, the increase magnification of peak strength also becomes small. When the amount of silica is not less than 6%, decreasing rate of specific surface area is not more than 10%, and the peak strength increases by 1.5 times or less.

In addition to silica-doped anatase titania, needle-like titanium oxide may be contained in the heat-resistant inorganic oxide layer. By virtue of the needle-like configuration, the needle-like titanium oxide acts to connect powdery heat resistant inorganic oxide particles integrally. Needle-like titanium oxides are tangled with each other randomly to define relatively large pores. The preferable average fiber diameter of these needle-like titanium oxides ranges from 0.01 to 1  $\mu\text{m}$ , and the preferable average fiber length thereof ranges from 1 to 6  $\mu\text{m}$ . And the preferable BET specific surface area ranges from 2 to 20  $\text{m}^2/\text{g}$ . The needle-like titanium oxide has SOx resistance, like the powdery titania, so that it can be used in an exhaust gas atmosphere containing a large amount of SOx for denitrification purpose, too.

Instead of the needle-like titanium oxide, zeolite can be used. Zeolite added to the heat-resistant inorganic oxide layer also acts to improve the purification performance of catalyst, like the needle-like titanium oxide.

The powdery heat-resistant inorganic oxide composing the heat-resistant inorganic oxide layer substantially supports catalyst metals. It is preferable that the powdery heat-resistant inorganic oxide has a large specific surface area and exhibits good activation, like the conventional one. The preferable average particle diameter of the powdery heat-resistant inorganic oxide ranges from 0.01 to 5  $\mu\text{m}$  and the preferable BET specific surface area thereof ranges from 50 to 500  $\text{m}^2/\text{g}$ .

To support the heat-resistant inorganic oxide layer with the catalyst substrate, it is preferable to prepare a slurry of the heat-resistant inorganic oxide and coat the catalyst substrate with the slurry prepared. Titania sol, or silica sol and aluminium nitrate, oxyzirconium nitrate or the like may be mixed as a binder when preparing the slurry. The preferable amount of coating of the heat-resistant inorganic oxide layer ranges from 50 to 250 g per unit volume (1 liter) of catalyst.

If the amount of coating of titania is less than 50 g, the catalytic property cannot be sufficiently achieved so as to be less preferable. If the amount of coating of titania exceeds 250 g, the amount of catalyst metal to be supported must be increased so as to be less preferable. The preferable average particle diameter of titania for composing the heat-resistant inorganic oxide layer ranges from 0.5 to 5  $\mu\text{m}$ , and the preferable content of titania containing silica in a resulting coating layer is 40 % or more.

The heat-resistant inorganic oxide layer can also support as a third component at least one of cesium, tungsten, molybdenum, vanadium, zirconium, yttrium, indium, cerium, praseodymium, copper, cobalt, gold, silver or the like. By virtue of the third component, the heat resistance of the catalyst is further improved, whereby the purification performance can be improved.

The preferable amount of platinum supported ranges from 0.1 to 5.0 g per unit volume (1 liter) of catalyst. If the amount of platinum supported exceeds 5.0 g/liter, the improvement of activation is very slight even with further increase of the amount of platinum so as to be expensive. In particular, 0.02 to 3.0 g/liter of platinum is more preferable for both the catalytic activation and cost.

The preferable amount of palladium supported ranges from 0.1 to 10.0 g per unit volume (1 liter) of catalyst. If the amount of palladium supported is less than 0.1 g/liter, sufficient catalytic activation may not be obtained. If the amount of palladium supported exceeds 10.0 g/liter, the improvement of activation is very slight even with further increase of the amount of palladium so as to be expensive. In particular, 0.5 to 5.0 g/liter of palladium is more preferable for both the catalytic activation and cost. When palladium is used along with platinum, the purification performance of the catalyst can be further enhanced.

The preferable amount of rhodium supported ranges from 0.01 to 1.0 g per unit volume (1 liter) of catalyst. If the amount of rhodium supported is less than 0.01 g/liter, sufficient catalytic activation may not be obtained. If the amount of rhodium supported exceeds 1.0 g/liter, the improvement of activation is very slight even with further increase of the amount of rhodium so as to be expensive. In particular, 0.05 to 0.5 g/liter of rhodium is more preferable for both the catalytic activation and cost.

These catalyst metals may be previously supported with titania powder containing silica to define the heat-resistant inorganic oxide layers. With this arrangement, the resistance to heat and poisonous components within exhaust gases can be both improved.

Since, with the catalyst of the present invention, silica-doped anatase titania is used in the heat-resistant inorganic oxide layer supporting the catalytic components, the particles defining the support layer are prevented from being enlarged due to sintering at elevated temperatures, whereby the heat-resistant inorganic oxide layer can maintain a large surface area, and accordingly, high catalytic performance can be maintained over a long period of time.

Other objects, features, and characteristics of the present invention will become apparent upon consideration of the following description and the appended claims, all of which form a part of this specification.

#### BRIEF DESCRIPTION OF THE DRAWINGS

The exact nature of this invention, as well as other objects and advantages thereof, will be readily apparent from consideration of the following specification relating to the annexed drawings in which:

Figure 1 is a diagram for showing the relationship between an amount of silica in silica-doped anatase titania and decreasing rate of specific surface area after a heat resistance test is performed;

Figure 2 is a diagram for showing the relationship between an amount of silica in silica-doped anatase titania and an increase magnification of peak strength on X-ray diffraction analysis after a heat-resistance test is performed.

#### DETAILED DESCRIPTION OF THE PRESENTLY PREFERRED EXEMPLARY EMBODIMENTS

Hereinafter, the present invention will be explained in detail based on several embodiments. The scope of the present invention is not limited to these embodiments.

##### Preparation of silica-doped titania powder:

Titanium tetrachloride (equivalent to 80 parts by weight of titanium dioxide) was dispersed in 500 parts by volume of isopropyl alcohol. Next, ethyl silicate (equivalent to 12 parts by weight of silica) was mixed with the alcohol solution thus prepared, and stirred for about 1 hour. Then, an aqueous solution composed of 50 parts by volume of 0.1N hydrochloric acid and 450 parts by volume of ion-exchange water was added to the above mixture at a rate of 1 ml/min. while stirring. This results in white colloid composed of silica-doped titania being formed due to hydrolysis reaction. After stirring for all day and night, the mixture was left for two days to grow the white colloid and resulting white precipitation was filtered.

After removing water at 120 °C, a product was fired at 700 °C for 1 hour. Upon examining the physical properties of resulting white powder (hereinafter will be called HST), a specific surface area was 90 m<sup>2</sup>/g, and an average particle diameter was 0.5 μm. Upon X-ray diffraction (hereinafter will be called XRD) analysis, the HST had a structure of anatase titanium dioxide. Upon quantitative analysis with fluorescent X ray, the amount of SiO<sub>x</sub> was 11 % by weight.

In the preparation described above, a sol-gel method based on alkoxide hydrolysis was used. Instead, other preparation methods such as a CVD method, coprecipitation method, flaming method or the like may be used.

#### Embodiment 1:

50 parts of HST powder thus prepared, 30 parts of mordenite of proton-type synthetic zeolite (silica-alumina ratio: about 30), 20 parts (in terms of solid portion) of titania sol STS-01 manufactured by Ishihara Sangyo and 100 parts of ion-exchange water were mixed together, and pulverized for 12 hours with a ball mill to prepare a slurry having an average particle diameter of 12 μm.

A monolith substrate formed of cordierite, which defines cells of 400 /in<sup>2</sup> and has a diameter of 117 mm and a length of 122 mm (volume: about 1.3 L), was coated with the slurry thus prepared. Then, the substrate was dried at 100 °C for 5 hours and heated at 250 °C for 3 hours to form a titania based heat-resistant inorganic oxide layer containing zeolite on the monolith substrate. The amount of a coating of the resultant heat-resistant inorganic oxide layer was 150 g per liter of the substrate (hereinafter will be disclosed 150g/L).

Next, the monolith substrate thus obtained was immersed in an aqueous solution containing a predetermined amount of platinum ammine hydrate. After excess water was blown off, the substrate was heated at 250 °C to decompose platinum salt to support 1.5 g of platinum per liter of substrate (hereinafter will be disclosed 1.5 g/L) with the substrate. Thus, a catalyst shown in Table 1 was obtained.

#### Embodiment 2:

A catalyst was prepared by the method similar to that of Embodiment 1 except that needle-like titanium oxide powder having an average fiber diameter of 0.07 to 0.5 μm and an average fiber length of 1 to 7 μm was added instead of mordenite. The average particle diameter of the slurry was 1 μm.

#### Embodiment 3:

A catalyst was prepared by the method similar to that of Embodiment 1 except that ZSM-5 obtained by ion-exchange of about 0.5 % by weight of cerium (Ce) was added instead of mordenite.

#### Embodiment 4:

A catalyst was prepared by the method similar to that of Embodiment 1 except that ZSM-5 obtained by ion-exchange of about 3.5 % by weight of cobalt (Co) was added instead of mordenite.

#### Embodiment 5:

A catalyst was prepared by the method similar to that of Embodiment 1 except that ZSM-5 obtained by ion-exchange of about 3.5 % by weight of copper (Cu) was added instead of mordenite.

#### Embodiment 6:

A catalyst was prepared by the method similar to that of Embodiment 1 except that USY (stable Y type zeolite) obtained by ion-exchange of about 0.5 % by weight of indium (In) was added instead of mordenite.

#### Embodiment 7:

After supporting platinum by the method similar to that of Embodiment 1, a substrate was immersed in an aqueous solution containing iridium chloride, and excess water was blown off. Then, the substrate was reduced within a hydrogen stream at 500 °C for 1 hour. The amount of iridium supported was 1g/L.

Next, the substrate was immersed in an aqueous solution containing cesium nitrate to support cesium nitrate with a heat-resistant inorganic oxide layer. After excess liquid was blown off, the substrate was dried at 250 °C and fired at 500 °C for 1 hour. The amount of cesium supported was 0.05 mol/L.

## Embodiment 8:

A catalyst was prepared by the method similar to that of Embodiment 7 except that rhodium chloride was used instead of iridium. The amount of rhodium was 0.2 g/L.

## Embodiment 9:

A catalyst was prepared by the method similar to that of Embodiment 7 except that palladium nitrate was used instead of iridium. The amount of palladium was 0.5 g/L.

## Embodiment 10:

A catalyst was prepared by the method similar to that of Embodiment 7 except that K-type ferrielite (silica-alumina ratio: about 20) was used instead of mordenite.

## Embodiment 11:

A heat-resistant inorganic oxide layer was formed on a substrate by the method similar to that of Embodiment 1, and then immersed in an aqueous solution containing ammonium metawolframate and ammonium molybdate. After excess water was blown off, the substrate was dried at 250 °C and fired at 500 °C for 1 hour. The amounts of W and Mo supported were 0.05 mol/L, respectively, in terms of elements thereof.

## Embodiment 12:

A catalyst was prepared by the method similar to that of Embodiment 11 except that an aqueous solution of oxalic acid of vanadium was used instead of the aqueous solution of ammonium metawolframate and ammonium molybdate. The amount of vanadium supported was 0.1 mol/L.

## Embodiment 13:

A catalyst was prepared by the method similar to that of Embodiment 11 except that zirconium oxynitrate was used instead of ammonium metawolframate and ammonium molybdate. The amount of zirconium supported was 0.1 mol/L.

## Embodiment 14:

A catalyst was prepared by the method similar to that of Embodiment 11 except that an aqueous solution of yttrium nitrate was used instead of ammonium metawolframate and ammonium molybdate. The amount of yttrium supported was 0.1 mol/L.

## Embodiment 15:

A catalyst was prepared by the method similar to that of Embodiment 11 except that an aqueous solution of praseodymium nitrate was used instead of ammonium metawolframate and ammonium molybdate. The amount of praseodymium supported was 0.1 mol/L.

## Embodiment 16:

A catalyst was prepared by the method similar to that of Embodiment 11 except that an aqueous solution of gold chloride was used instead of ammonium metawolframate and ammonium molybdate. The amount of gold supported was 0.1 g/L.

## Embodiment 17:

A catalyst was prepared by the method similar to that of Embodiment 11 except that an aqueous solution of silver nitrate was used instead of ammonium metawolframate and ammonium molybdate. The amount of silver supported was 0.1 mol/L.

## Embodiment 18:

A catalyst was prepared by the method similar to that of Embodiment 1 except that silica-doped anatase titania obtained by the reaction of evaporated titanium tetrachloride and evaporated silicon tetrachloride in an atmosphere containing of inert gas, air and hydrogen with a flame from a burner (flaming method) was used instead of HST powder. This silica-doped anatase titania had a BET specific surface area of  $56 \text{ m}^2/\text{g}$ , an average particle diameter of  $4 \text{ }\mu\text{m}$ , and a structure of anatase titanium dioxide. The content of  $\text{SiO}_2$  measured with fluorescent X ray was 8 % by weight.

## Embodiment 19:

A catalyst was prepared by the method similar to that of Embodiment 1 except that 30 parts of HST powder was added instead of 30 parts of mordenite powder.

## Comparative example 1:

A slurry composed of 100 parts by weight of activated alumina powder having an average particle diameter of  $5 \text{ }\mu\text{m}$ , 5 parts by weight of alumina hydration, 1 part by weight of aluminium nitrate and 150 parts by weight of ion-exchange water was applied to a monolith substrate formed of cordierite, which defines cells of  $400/\text{in}^2$  and has a diameter of 117 mm and a length of 122 mm (volume of about 1.3 L). Then, the substrate was dried and fired at  $500 \text{ }^\circ\text{C}$  for 1 hour to form a heat-resistant inorganic oxide layer ( $150 \text{ g/L}$ ) composed of an activated alumina layer on the monolith substrate.

Next, the monolith substrate provided with the heat-resistant inorganic oxide layer was immersed in an aqueous solution of dinitrodiamino platonic acid to support  $1.5 \text{ g/L}$  of platinum.

## Comparative sample 2:

A catalyst was prepared by the method similar to that of Comparative example 1 except that 100 parts by weight of titanium dioxide powder having an average particle diameter of  $3 \text{ }\mu\text{m}$  and titania sol STS-01 (equivalent to 20 parts by weight of titanium dioxide) were used instead of activated alumina powder and alumina hydration.

## Comparative example 3:

A catalyst was prepared by the method similar to that of Comparative example 2 except that 90 parts by weight of titanium dioxide powder and 10 parts by weight of silicapowder were used in place of 100 parts by weight of titanium dioxide powder.

## Comparative example 4:

A catalyst was prepared by the method similar to that of Comparative example 2 except that anatase titanium dioxide containing 9 % by weight of alumina and having a BET specific surface area of  $88 \text{ m}^2/\text{g}$ , which was prepared by the flaming method disclosed in Japanese Patent No. 2503370, was used instead of titanium dioxide powder.

## Comparative example 5:

A catalyst was prepared by the method similar to that of Comparative example 2 except that 60 parts by weight titanium dioxide powder, 10 parts by weight of silica powder and 30 parts by weight of mordenite powder were used instead of 100 parts by weight of titanium dioxide powder.

## Endurance and evaluation method:

Catalysts thus prepared were respectively secured to a DI turbo-engine of 3.1 liter. And the engine was operated for 500 hours with repetition of cycles, each being composed of 10 minutes of idle operation and 10 minutes of operation at 2000 rpm with 40 % load (inlet gas temperature:  $400 \text{ }^\circ\text{C}$ ) and then operated for 50 hours under full-throttled condition at 4000 rpm (inlet gas temperature:  $670 \text{ }^\circ\text{C}$ ). Thus, endurance samples were prepared.

Samples thus prepared were respectively secured to a DI turbo-vehicle of 2.8 liter, and Japanese 10 Mode and 15 Mode were measured with a Chassis dynamometer and Dilution tunnel manufactured by Horiba Seisakusho to examine the relation between the purification performance against HC, CO, NOx and PM and catalysts.

Next, samples were removed from the vehicle, and the coating layers were scratched off. Then, the state of each

sample was examined with respect to the rate of deterioration of BET specific surface area (D) and XRD thereof. Table 1 shows the components of each sample and Table 2 shows the rate of purification and state thereof. In Table 2, "initial" means the catalyst of Embodiment 1 prior to endurance tests.

Table 1

Embodiment No.	Composition of heat-resistant inorganic oxide layer				Catalyst metal		Amount of inorganic oxide layer
	A group	B group	C group	additive	kind	amount (g/L)	amount of coating(g/L)
1	silica-doped titania	mordenite	titania sol	-	Pt	1.5	150
2	silica-doped titania	needle like titania	titania sol	-	Pt	1.5	150
3	silica-doped titania	ZSM-5	titania sol	Ce	Pt	1.5	150
4	silica-doped titania	ZSM-5	titania sol	Co	Pt	1.5	150
5	silica-doped titania	ZSM-5	titania sol	Cu	Pt	1.5	150
6	silica-doped titania	USY	titania sol	In	Pt	1.5	150
7	silica-doped titania	mordenite	titania sol	Cs	Pt/Ir	1.5/1	150
8	silica-doped titania	mordenite	titania sol	Cs	Pt/Rh	1.5/0.2	150
9	silica-doped titania	mordenite	titania sol	Cs	Pt/Pd	1.5/0.5	150
10	silica-doped titania	ferrielite	titania sol	Cs	Pt/Ir	1.5/1	150
11	silica-doped titania	mordenite	titania sol	W/Mo	Pt	1.5	150
12	silica-doped titania	mordenite	titania sol	V	Pt	1.5	150
13	silica-doped titania	mordenite	titania sol	Zr	Pt	1.5	150
14	silica-doped titania	mordenite	titania sol	Y	Pt	1.5	150
15	silica-doped titania	mordenite	titania sol	Pr	Pt	1.5	150
16	silica-doped titania	mordenite	titania sol	Au	Pt	1.5	150
17	silica-doped titania	mordenite	titania sol	Ag	Pt	1.5	150
18	silica-doped titania	mordenite	titania sol	-	Pt	1.5	150
19	silica-doped titania	-	titania sol	-	Pt	1.5	150
Comparative ex.							
1	alumina	-	alumina hydration	-	Pt	1.5	150
2	titania	-	titania sol	-	Pt	1.5	150
3	silica-doped titania	-	titania sol	-	Pt	1.5	150
4	titania, alumina	-	titania sol	-	Pt	1.5	150
5	titania, silica	-	titania sol	-	Pt	1.5	150



Table 2

Embodiment No.	Rate of purification (%)				State of catalyst layer	
	HC	CO	NOx	PM	D(%)	XRD
1	83	81	13	46	4	anatase TiO <sub>2</sub> , mordenite
2	85	80	18	45	3	anatase TiO <sub>2</sub> , needle-like TiO <sub>2</sub>
3	82	80	19	45	5	anatase TiO <sub>2</sub> , ZSM-5
4	85	81	14	46	7	anatase TiO <sub>2</sub> , ZSM-5
5	80	82	16	42	8	anatase TiO <sub>2</sub> , ZSM-5
6	84	79	21	40	7	anatase TiO <sub>2</sub> , USY
7	86	83	17	43	2	anatase TiO <sub>2</sub> , mordenite
8	87	82	16	43	4	anatase TiO <sub>2</sub> , mordenite
9	79	80	12	42	5	anatase TiO <sub>2</sub> , mordenite
10	80	79	13	41	8	anatase TiO <sub>2</sub> , mordenite
11	82	84	15	40	9	anatase TiO <sub>2</sub> , mordenite
12	83	84	19	45	4	anatase TiO <sub>2</sub> , mordenite
13	81	82	11	44	3	anatase TiO <sub>2</sub> , mordenite
14	81	81	13	43	2	anatase TiO <sub>2</sub> , mordenite
15	84	81	15	43	3	anatase TiO <sub>2</sub> , mordenite
16	83	81	14	40	0	anatase TiO <sub>2</sub> , mordenite
17	81	79	12	40	0	anatase TiO <sub>2</sub> , mordenite
18	79	79	13	47	2	anatase TiO <sub>2</sub> , mordenite
19	75	79	12	40	3	anatase
initial	85	86	21	45	4	
Comparative ex.1	43	65	0	20	40	partly aluminum sulfate
Comparative ex.2	47	67	-1	15	92	crystal (rutile)
Comparative ex.3	42	60	0	18	89	crystal (rutile)
Comparative ex.4	48	66	1	23	47	crystal
Comparative ex.5	53	67	3	29	45	crystal

As shown in Table 2, the rate of purification of each catalyst of the present invention was close to that of the initial catalyst prior to endurance tests. These results show that the deterioration of the catalysts of the present invention was very slight. In contrast, in the case of the comparative examples using neither mordenite nor needle-like titania, the rate of purification greatly decreased, and the rate of deterioration of the specific surface area (D) indicating the degree of the deterioration of the catalyst layer was remarkably increased. Upon examining the comparative examples with XRD, it was observed that the titania layer was changed to crystal (rutile) due to sintering. In contrast, in the use of the present embodiments, the rate of deterioration of the specific surface area (D) were small, and upon examining with XRD, titania was in the state of anatase in each embodiment. These results show that the catalysts of the present embodiments were substantially identical to the initial catalyst prior to endurance tests in their state and performance.

As described above, with the catalyst for purifying exhaust gases from diesel engines in accordance with the present invention, of which a heat-resistant inorganic oxidelayer contains as a main ingredient silica-doped titania and needle-like titanium oxide or zeolite, high purification performance against HC, CO, NOx and particulates, and good durability can be achieved even in high temperature atmospheres such as exhaust gases from diesel engines, which show that high catalytic property of silica-doped titania can be maintained, because the particles of the heat-resistant inorganic oxide layer supporting catalysts are not enlarged.

While the invention has been described in connection with what are considered presently to be the most practical and preferred embodiments, it is to be understood that the invention is not limited to the disclosed embodiments, but, on the contrary, is intended to cover various modifications and equivalent arrangements included within the spirit and scope of the appended claims.

A catalyst for purifying exhaust gases, which is capable of maintaining the catalytic property and purification performance against particulates, HC, CO and NO<sub>x</sub> over a long period of time. The catalyst has a catalyst substrate and a heat-resistant inorganic oxide layer containing catalytic components, which is provided on the catalyst substrate. The heat-resistant inorganic oxide layer contains silica-doped anatase titania having a structure that 3 to 35 % by weight of silica is finely dispersed between and retained by anatase titania particles, which is an oxide obtained in the state where a silicon-containing compound and titanium-containing compound are mixed in the molecular state.

## Claims

1. A catalyst for purifying exhaust gases, comprising:

a catalyst substrate; and  
a heat-resistant inorganic oxide layer containing catalytic components, which is provided on said catalyst substrate, said heat-resistant inorganic oxide layer containing silica-doped anatase titania having a structure that 3 to 35 % by weight of silica is finely dispersed between and retained by anatase titania particles, which is an oxide obtained in the state where a silicon-containing compound and titanium-containing component are mixed in the molecular state.

2. A catalyst as claimed in claim 1, wherein said silica-doped anatase titania has a BET specific surface area of 50 to 200 m<sup>2</sup> /g which decreases by 10 % or less due to heat treatment in air at 800 °C for 5 hours.

3. A catalyst as claimed in claim 1, wherein the peak strength cps of said silica-doped anatase titania upon X-ray diffraction analysis with  $2\theta = 25^\circ$  increases by 1.5 times or less due to heat treatment in air at 800 °C for 5 hours.

4. A catalyst as claimed in claim 1, wherein said catalytic components include at least one of platinum, palladium and rhodium.

5. A catalyst for purifying exhaust gases, comprising:

a catalyst substrate; and  
a heat-resistant inorganic oxide layer containing catalytic components, which is provided on said catalyst substrate, said heat-resistant inorganic oxide layer being composed of a silica-doped anatase titania layer having a structure that 3 to 35 % by weight of silica is finely dispersed between and retained by anatase titania particles, which is an oxide obtained in the state where a silicon-containing compound and titanium-containing compound are mixed in the molecular state, and at least one catalytic component selected from the group consisting of platinum, palladium and rhodium.

6. A catalyst as claimed in claim 5, wherein said catalyst purifies exhaust gases discharged from diesel engines.

7. A catalyst as claimed in claim 6, wherein said silica-doped anatase titania has a BET specific surface area of 50 to 200 m<sup>2</sup> /g which decreases by 10 % or less due to heat treatment in air at 800 °C for 5 hours.

8. A catalyst as claimed in claim 6, wherein the peak strength cps of said silica-doped anatase titania upon X-ray diffraction with  $2\theta = 25^\circ$  increases by 1.5 times or less due to heat treatment in air at 800 °C for 5 hours.

9. A catalyst for purifying exhaust gases comprising:

a catalyst substrate;  
a heat-resistant ceramic layer supporting catalytic components, which is provided on said catalyst substrate, said heat-resistant ceramic layer containing silica-doped anatase titania powder having a structure that 3 to 35 % by weight of silica is finely dispersed between and retained by anatase titania particles, which is an oxide obtained in the state where a silicon-containing compound and titanium-containing compound are mixed in the molecular state, and needle-like titanium oxide such that 100 % by weight of said heat-resistant ceramic layer contains 5 to 80 % by weight of needle-like titanium oxide, said needle-like titanium oxide being dispersed in

said heat-resistant ceramic layer randomly.

10. A catalyst as claimed in claim 9, wherein said catalyst purifies exhaust gases discharged from diesel engines.
- 5 11. A catalyst as claimed in claim 10, wherein said silica-doped anatase titania has a BET specific surface area of 50 to 200 m<sup>2</sup>/g which decreases by 10 % or less due to heat treatment in air at 800 °C for 5 hours.
12. A catalyst as claimed in claim 10, wherein the peak strength cps of said silica-doped anatase titania upon X-ray diffraction analysis with  $2\theta \approx 25^\circ$  increases by 1.5 times or less due to heat treatment in air at 800 °C for 5 hours.
- 10 13. A catalyst as claimed in claim 10, wherein said silica-doped anatase titania powder has an average particle diameter of 0.01 to 50 μm and a BET specific surface area of 50 to 200 m<sup>2</sup>/g, said needle-like titanium oxide has an average fiber diameter of 0.01 to 1 μm and a fiber length of 0.5 to 30 μm.
- 15 14. A catalyst for purifying exhaust gases comprising:
  - a catalyst substrate;
  - a heat-resistant ceramic layer supporting catalytic components, which is provided on said catalyst substrate, said heat-resistant ceramic layer containing silica-doped anatase titania powder having a structure that 3 to 35
  - 20 % by weight of silica is finely dispersed between and retained by anatase titania particles, which is an oxide obtained in the state where a silicon-containing compound and titanium-containing compound are mixed in the molecular state, and zeolite such that 100 % by weight of said heat-resistant ceramic layer containing 5 to 80 % by weight of zeolite, said zeolite being dispersed in said heat-resistant ceramic layer randomly.
- 25 15. A catalyst as claimed in claim 14, wherein said catalyst purifies exhaust gases discharged from diesel engines.
16. A catalyst as claimed in claim 15, wherein said silica-doped anatase titania has a BET specific surface area of 50 to 200 m<sup>2</sup>/g which decreases by 10 % or less due to heat treatment in air at 800 °C for 5 hours.
- 30 17. A catalyst as claimed in claim 15, wherein the peak strength cps of said silica-doped anatase titania upon X-ray diffraction with  $2\theta \approx 25^\circ$  increases by 1.5 times or less due to heat treatment in air at 800 °C for 5 hours.
18. A catalyst as claimed in claim 15, wherein said silica-doped anatase titania powder has an average particle diameter of 0.01 to 50 μm and a BET specific surface area of 50 to 200 m<sup>2</sup>/g, said zeolite is ferrielite-type, pentasilite-type (ZSM-5), mordenite-type, Y-type zeolite, and has an average particle diameter of 0.1 to 50 μm.
- 35 19. A catalyst as claimed in claim 19, wherein said catalytic components include at least one of palladium, rhodium and iridium.
- 40 20. A catalyst as claimed in claim 15, wherein said catalytic components include at least one of Cs, W, Mo, V, Zr, Y, In, Ce, Pr, Cu, Co, Au and Ag as an additive.

FIG. 1

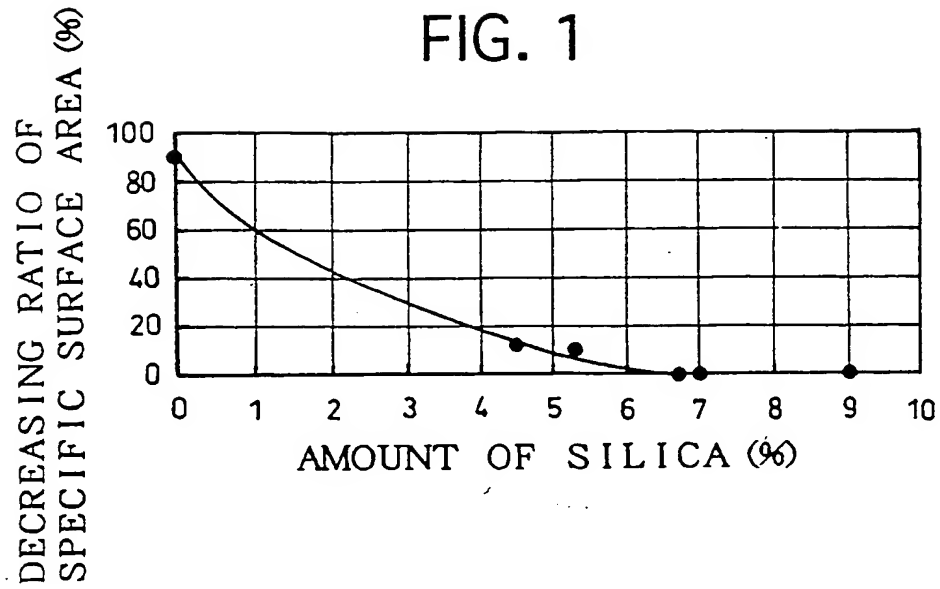


FIG. 2

